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Semi-Empirical Mass Balance Approach for Estimating Primary Emissions of Reactive Species from an Urban-Industrial Complex

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A SEMI-EMPIRICAL MASS BALANCE APPROACH FOR ESTIMATING PRIMARY EMISSIONS OF REACTIVE SPECIES FROM AN URBAN-INDUSTRIAL COMPLEX

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16. ABSTRACT

More than half of the U.S. anthropogenic emissions of NO_x, and more than three-quarters of the corresponding VOC emissions, are from area sources, mostly concentrated in urban areas. There is significant evidence that current estimates of these emissions may be substantially in error. These estimates are critical inputs to the new complex regional Eulerian models developed for policy analysis, and will be the target of control strategies for abatement of such air pollution problems as regional haze, acidic deposition, and oxidants. Direct methods for testing the accuracy of some area source emissions estimates are impractical, particularly for VOC. We seek indirect methods based on ambient measurements.

A semi-empirical mass balance method for indirect estimation of urban NO_x and VOC emissions is described in this paper. It requires measurement of ambient concentrations of these precursors at urban inflow and outflow boundaries and of the local wind field. In the mass balance, the effect of chemical transformations and removal of the mass balance species (primary as well as secondary) is estimated by means of a crosswind-resolved reactive plume model. As part of an on-going EPA-sponsored project, the method will be applied to existing field data of four eastern U.S. urban areas. The existing data bases were not developed for the present purpose, and are much less than ideal. The outline of a design field study specifically aimed at the current objectives is also described.

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INTRODUCTION

Acid deposition, regional haze, and photochemically-produced oxidants are among the principal problems of concern in regional air pollution in eastern North America. Major efforts are under way both in the U.S. and in Canada to develop complex regional Eulerian models (e.g. RADM, ADOM, ROM) aimed at assessing these problems, and at development of rational strategies for their control. The principal cause of these problems, and the target of their control, is the anthropogenic emission of the precursors SO_x, NO_x, and VOC (volatile organic compounds). Sufficiently accurate quantitative specification of these emissions, and a reliable estimation of the uncertainty associated with the emissions inputs, are of crucial importance to the credibility of model outputs which will shape policy formulation and implementation. The uncertainty associated with the current emissions inventory data of NO_x and VOC, in particular, is thought to be larger than the degree of maximum anticipated control of these pollutants.[1] This uncertainty is particularly large for area source emissions which are believed to contribute about half of the U.S. anthropogenic emissions of NO_x, and more than three-quarters of the emissions of VOC. Vehicular exhaust is the dominant area source of NO_x, and a major area source of VOC also. About half of all the known VOC area-source emissions are commonly lumped as "miscellaneous", a category dominated by evaporative emissions from organic solvents. Accurate direct estimation of the strength of such emissions is practically impossible. Indirect reliable techniques for testing the accuracy of current emissions estimates are urgently needed.

The area source emissions of NO_x and VOC are substantially concentrated in urban-industrial complexes. Urban emission inventories of these precursors thus take on particular significance. Urban areas differ greatly in terms of their source distributions of these precursors. For example, the ratio of area-source to major point-source emissions of NO_x, based on the current emissions inventory, is about 1:1 for the whole U.S., less than 1:? for St. Louis , and more than 5:1 for Atlanta. Any generalizations based on analyses of emissions from selected urban areas must, therefore, be resolved at the level of specific categories of sources rather than at the scale of the entire urban source. Appropriate methodologies for data analysis developed based on data of specific metropolitan areas may, however, be applied more generally.

There are at least two indirect approaches for estimating urban emissions of VOC and NO_x based on ambient measurements: tracer methods and the mass balance method. An EPA-sponsored research project was recently initiated at Washington University with the following main goals:

a) to formulate the mass balance method, and to apply it to *existing* field data of up to four urban areas in eastern North America to assess its utility and reliablility in estimating NO_x and VOC emissions (urban aggregate, as well as source-segregated);
b) to compare the mass balance emission estimates with those based on the existing emissions inventory; and,
c) to formulate the design of a future field study aimed specifically at estimating urban NO_x and VOC emissions and their uncertainties based on the mass balance and tracer methods.

An overview of EPA's objectives and approach related to the above project is given in a companion paper[1]. In our paper, we focus more on the mass balance method itself, and its application. The mass balance explicitly includes the precursors and their reaction products. The method is semi-empirical, involving the use of measured ambient concentrations of the precursor species (and of the products, where available) at sections upwind and downwind of the urban source area. Also, empirical data of the local flow field are needed. A mass balance

of the precursors between the two sections is used to infer their emissions from the urban source. The roles of chemical transformations and removal of the precursors between emission and downwind sampling are simulated by the use of a reactive plume model with appropriate spatial/temporal resolution. In this paper, we present the outlines of our mass balance and plume model formulations, and of the manner of their application based on existing (non-ideal) as well as future (more nearly ideal) field data bases. The four specific existing urban data bases selected for actual use in the application phase of the project are briefly described, noting their strengths and expected shortcomings. The principal criteria for an appropriate field study design specific to estimation of urban NO_x and VOC emissions (and of the associated uncertainty), based on the mass balance method, are also outlined.

PERTINENT BACKROUND

Significance of NOx-VOC Atmospheric Chemistry

The complex and non-linear atmospheric photochemistry of NO_x and VOC plays a particularly important role in air pollution. Complex chains of reactions are initiated when photochemically generated HO, O, and O_3 cause the breakdown of the VOC, leading to the production of various free radical species (e.g. HO, HO_2, RO_2, $RCOO_2$). These, in turn, cause the oxidation of SO_2-to-sulfates, NO-to-NO_2, NO_x-to-nitrates (including organic nitrates such as PAN), and the production of oxidants such as O_3 and H_2O_2. These oxidants themselves also play an important role in the oxidation of SO_2 in the liquid phase. The SO_x-NO_x-VOC atmospheric chemistry plays a critical role in shaping the spatial-temporal distribution of acidic deposition, regional haze, and photochemical smog, by virtue of the fact that the atmospheric residence times of the precursors and of their reaction products are generally very different.

Besides the absolute magnitudes of NO_x and VOC emissions, two other aspects pertaining directly to these precursor emissions also have an important influence on the nature of the NO_x-VOC chemistry: the magnitude and spatial distribution of the ratio VOC/NO_x, and the chemical composition of the VOC emissions. Depending on whether the value of VOC/NO_x is larger or smaller than a critical range, the chemistry will be either predominantly NO_x-limited or predominantly VOC-limited, respectively. This fact has important implications concerning the strategy for controlling secondary pollution formation (e.g. oxidants). The VOC/NO_x ratio in a plume generally changes continuously as the plume mixes with other plumes, and as it dilutes into the regional background. For plumes which are deficient in VOC (e.g. fresh power plant plumes), the chemistry is thus diffusion-limited[2]. The spatial resolution of any model simulations is thus an additional factor contributing to uncertainty. Owing to the importance of the VOC/NO_x ratio, the uncertainty of model simulations will depend not only on the uncertainty of VOC and NO_x emissions individually, but rather on the combined uncertainty of both. Furthermore, VOC are comprised of many individual species whose reactivities in the above chemistry vary over a broad range. It is thus necessary to obtain reliable emissions estimates for the individual VOC species. This is particularly difficult for the more reactive ones. In practice, the more detailed VOC emissions inventories are based on groupings of VOC species based on four reactivity classes (paraffins, aromatics, olefins, and aldehydes). The more sophisticated models typically involve dozens of VOC species, the emission estimates for which are derived by disaggregation of coarser data.

Urban emissions of NO_x and VOC also play an important role in the chemistry of rural emissions of SO_x and NO_x (e.g. from rural power plants). In general, the depletion of NO_x in an urban plume is more rapid than the depletion of VOC. In an aged urban plume, when the NO_x is mostly depleted, significant VOC remains and contributes to a relative abundance of VOC in

the rural background. Such excess VOC in the regional background plays a controlling role in the chemistry of rural emissions of SO_x and NO_x from point sources such as power plants[3].

Reliability of Current Urban Emission Estimates of NO_x and VOC

The overall uncertainty of current urban emission estimates of NO_x and VOC is a result of the compounding of uncertainties pertaining to source identification, source configuration, source strength, and the spatial, temporal, and species resolutions of the emissions. Source strength itself is commonly derived from information related to emission factors, source activity levels, and control equipment performance. Attempts have been made to assess the uncertainties associated with each of these various contributing components, and in many cases, these have individually been estimated to be as high as 100%.[4] When compounded, the overall uncertainties, in some cases, leave little confidence in the corresponding data of the emissions inventory. Attempts have therefore been made to assess, at least in a gross way, the reliability of the aggregate urban emission estimates by indirect methods based on ambient concentration measurements.

About 1375 state-of-the-art measurements of ambient concentrations of NO_x and VOC were made in the summer of 1984 at a number of urban sites in 14 different cities in the eastern U.S., as well as in Kansas City, MO and 7 cities in Texas.[5] For the eastern U.S. cities, the median urban values of the *ambient concentration* ratio, VOC/NO_x, ranged between 8 and 20, with the median of medians being about 12. In contrast, the value of this ratio (in comparable molar units) based on the *emissions inventory* ranges between about 3 for eastern U.S. urban counties with the highest NO_x emissions flux, and 4 for urban counties with the highest VOC emissions flux. In an independent study in Atlanta[6], the indication was that the urban ambient concentration ratio (VOC/NO_x) was about five times greater than the corresponding emissions inventory ratio. In that study, it was also demonstrated through model calculations that the discrepancy was almost entirely attributable to a five-fold underestimation in the VOC emissions inventory. While the ambient concentration ratio (VOC/NO_x) is expected to be larger than the emissions ratio owing to the faster chemical depletion of NO_x by chemical transformations between the source and the receptor [7], the size of the discrepancy (factor of 3 to 5) is disconcertingly large when the receptor sites are practically within the source field.

In a very different approach, an attempt was made to characterize the chemical composition of the regional background in the Midwest based on field data and model simulations of the observed dynamics of ozone production simultaneously in an isolated power plant plume and in its background[3]. Since ozone production in the power plant plume (low VOC/NO_x) is controlled by background VOC and plume dilution, and that in the background (high VOC/NO_x) is controlled by background NO_x, this approach of *background* characterization is an exacting one simultaneously with respect to both NO_x and VOC. The result of the study was that the inferred background NO_x was consistent with the standard regional anthropogenic emissions estimates of NO_x, but the same was not true for VOC. For "proper" background VOC (in the context of plume ozone production), it was necessary to invoke a regional emissions strength about four times greater than that based on the current inventory of anthropogenic VOC emissions. It was speculated that the discrepancy was probably due to a combination of underestimation in the anthropogenic emission inventory and non-negligibility of the natural emissions of VOC. While the conclusions of the above studies are suggestive, at best, concerning the reliability of the VOC emissions estimates, their implications are potentially serious. What if actual anthropogenic VOC emissions *are* two or three times higher than current estimates? Further assessment and improvement of the current emissions inventory, particularly for VOC, are clearly needed, and must precede, or at least go hand in hand with, any massive efforts to generate and apply field data for the evaluation of regional

models for policy analyses.

THE MASS BALANCE METHOD

Historical Perspective

The mass balance concept has been applied in air quality studies to estimate the contributions of fresh emissions, chemical transformations, and scavenging processes based on observed changes in the air quality of Lagrangian air parcels. Since pollutant plumes are moving three-dimensional reaction media, appropriate applications of mass balance concepts depend upon 3-D sampling which is best accomplished in the atmosphere by way of aircraft measurements. A pioneering study aimed at reconciliation of aircraft measurements of air pollutants with source emissions was applied to the data of CO and light-scattering aerosol collected as part of the 1972-73 3-D Gradient Study in the Los Angeles basin[8]. Also, from the data of winds aloft and measured aircraft data of ozone, a *mass flow rate* (m) for the export of ozone to the east was calculated according to the formula

$$\dot{m}(x) \equiv \int_0^{\infty} \int_{-\infty}^{+\infty} u(x,z) \cdot C_e(x,y,z)\, dy\, dz \quad , \qquad (1)$$

where u denotes the local, instantaneous wind speed, and

$$C_e(x,y,z) = C(x,y,z) - C_b(x,z) \qquad (2)$$

denotes the local excess concentration field over the local background concentration, C_b. x, y, z refer, respectively, to the downwind, crosswind, and vertical space co-ordinates. It was noted in the Los Angeles study that a direct interpretation of the mass flow rate value for ozone in terms of precursor emission rates was confounded by the unsteady nature of the local transport winds.

The mass balance concept was later adopted as a basis for the design of the Midwest Interstate Sulfur Transport and Transformation (MISTT) field measurements in 1974-76. The goal was to extract information concerning rates of SO_x chemical transformations and ground removal between successive quasi-Lagrangian downwind sections in urban and power plant plumes, based on observed changes in the cross-sectional mass flow rates calculated using measured aircraft data of SO_2 and sulfate concentrations, and the measured wind data. Such measurements and analyses provided estimates of total SO_2 loss rates in pollutant plumes[9], and information related to the formation of ozone and light-scattering aerosol in the urban plume of St. Louis[10]. Uneasiness continued to prevail, however, concerning the use of instantaneous cross-sectional wind speeds in the analyses. In subsequent MISTT data analyses and diagnostic modeling,[11, 12] the following cross-sectional mass-related empirical quantity was used in data interpretation:

$$M(x) \equiv \int_0^{\infty} \int_{-\infty}^{+\infty} C_e(x,y,z)\, dy\, dz \qquad (3)$$

M(x) is simply the excess pollutant mass per unit downwind depth in a vertical plume slab at cross-section x, and it is independent of the local instantaneous wind speed. Later still, the concept of the *virtual emission rate*, Q_0^*, defined as:

$$Q_0^*(x) = U_0 \cdot \int_0^{\infty} \int_{-\infty}^{+\infty} C_e(x,y,z)\, dy\, dz \qquad (4)$$

was introduced.[13] Here U_0 represents the mean transport wind averaged *over the emission domain* during the period of passage through it of the Lagrangian air parcel sampled at x. Observe that

$$Q_0^* = U_0 \cdot M \qquad (5)$$

Q_0^* was designed as a quantity related to emissions, and, like M(x), is independent of the unsteadiness of u(x). Q_0^* also represents the steady-state *emission rate* of an inert species which would account for the observed concentration field at x. For purely secondary, non-conservative species such as ozone, it provides a measure of the average *rate of production* of the species over the transport time to x. The validity of Q_0^* as a surrogate for the emission rate of conservative precursor species, or for the production rate of secondary species, is based on the assumption that the wind field remains steady and uniform over the source domain during the appropriate period of emission. For a large urban source, this period may be several hours. Our mass balance formulation, outlined below, avoids making this same assumption.

Metropolitan Scale Mass Balance --- Formulation

With reference to Figure 1, consider the Lagrangian passage of a semi-infinite vertical slab, Γ, between crosswind sampling sections upwind (x_u) and downwind(x_d) of an urban source complex. The slab is defined to have *fixed* thickness δx in the downwind direction. At time t, the front edge of the slab is at x(t) (the figure shows the slab at $t+\delta t$). The source area is characterized, in general, by a spatially non-uniform and temporally variable pattern of surface emission flux, q(x, y, t), of any arbitrary primary species. Q(t) denotes the spatially aggregated emission rate of the species for the whole source area.

The *differential* mass balance for any arbitrary species in the slab during time δt, as the slab moves through a distance δx over the source region, may be expressed as follows:

$$m(\Gamma:t+\delta t) - m(\Gamma:t) = \dot{m}_s(\Gamma:t)\delta t + \dot{m}_k(\Gamma:t)\delta t \qquad (6)$$

where $m(\Gamma:t) = \delta x \cdot M(x)$ = species mass content of slab at time t; $\dot{m}_s$ and $\dot{m}_k$ denote the rates of species mass contributions to the slab during δt due, respectively, to source emissions and kinetics (chemical transformations and removal). Integrating equation (6) over the period between t_u and t_d (respectively, the times when the slab arrives at the upwind and downwind sections at x_u and x_d), the *integral* mass balance for arbitrary species i, between the upwind and downwind sections can be shown to be

$$\left\langle \frac{Q}{u_0} \right\rangle_j = \left[M(x_d) - M(x_u) \right]_j - P_{kin,j} \qquad \text{for species j,} \qquad (7)$$

where $\left\langle \frac{Q}{u_0} \right\rangle_j \equiv \int_{-\infty}^{\infty} \int_{x_u}^{x_d} \left(q/u_0 \right)_j \, dx \, dy$ is the source term,

and $P_{kin,j} \equiv \int_{t_u}^{t_d} \int_{0}^{\infty} \int_{-\infty}^{+\infty} \left(\frac{\partial C}{\partial t} \right)_{kin,j} dy \, dz \, dt$ is the kinetic production term

In the above equations, $u_0(x,t)$ denotes the current, slab-average magnitude of the transport wind speed as the slab passes over the source domain, and $(\partial C/\partial t)_{kin,j}$ denotes the spatial distribution of the rate of change of the concentration field of species j within the slab due to kinetic processes (chemistry and removal). Observe that the contribution of the local emission flux is weighted by the reciprocal of the local wind speed or, equivalently, by the local residence time of the slab over each emission grid cell. For proper evaluation of u_0, the current plume height, and local data of winds aloft to that height, are needed. This is potentially a source of significant uncertainty in the application of the mass balance method. Since the kinetics of all species are, in general, coupled through the complex non-linear reactive plume chemistry, the most appropriate way to estimate the kinetics term is by means of a detailed reactive plume model. Also, since the analysis is, by design, over a spatial size comparable to the size of the metropolitan area, one must presume that the spatial inhomogeneities of the emission field will cause significant variations in the chemistry. Consequently, the reactive plume model must possess an appropriate spatial resolution, which can be adapted to the city-specific distribution of precursor emissions. We have developed such a mesoscale, Lagrangian, reactive plume model with arbitrary crosswind resolution. It will be used to estimate $(\partial C/\partial t)_{kin}$ with that crosswind resolution at each integration time step for each species included in the model. P_{kin} can be obtained by spatially integrating $(\partial C/\partial t)_{kin}$ over the slab cross-section at each integration time step in the model run, and by further integrating such space integrals over the full run time of the model between t_u and t_d.

In the existing data bases, for a city such as St. Louis with an urban stretch approximating 50 km, it is not unusual for (x_d-x_u) to be about 100 km, and for (t_d-t_u) to be over 5 hours. Furthermore, most such data are available for summer days. Consequently, the magnitude of the kinetics term, particularly for the more reactive primary species, can be highly significant, and possibly even dominant.

In the above mass balance formulation (equation 7), the ΔM term on the right side is the empirical term to be determined from aircraft data of the precursor concentration fields at cross-sections x_u and x_d. Ideally, x_u and x_d should be immediately upwind and downwind of the urban source domain, so that the source term (left side of the equation) includes only the target urban source. In existing data bases, this is not generally the case, and frequently the nearest downwind sampling section is 30 km or more beyond the downwind edge of the urban source. For application to existing data bases, therefore, one may consider the breakdown of the source term as follows:

$$\left\langle \frac{Q}{u_0} \right\rangle = \left\langle \frac{Q}{u_0} \right\rangle_{urban} + \left\langle \frac{Q}{u_0} \right\rangle_{upwind} + \left\langle \frac{Q}{u_0} \right\rangle_{downwind} \quad (8)$$

where the three terms on the right side refer, respectively, to the sources within the urban area, and in the upwind and downwind stretches outside the urban area. Consequently, in order to estimate the contribution of the urban emissions, it is neccessary first to estimate the contribution of upwind and downwind emissions.

Cross Sectional Concentration Integration (The Empirical Term)

The empirical term in Equation (7) involves the evaluation of the cross-sectional integration, M(x), of the measured precursor concentration distribution, in excess of the background level, at the inflow and outflow sections. If the inflow distribution is the same as the regional background, then $M(x_u)=0$. The procedure outlined below pertains to the evaluation of $M(x_d)$ at any arbitrary downwind plume section. The illustration of the procedure is based on typical aircraft data of a continuously measured parameter such as NO_x or O_3 (O_3 data are used in the illustration presented in this section).

In many of the existing field data bases, the aircraft measurements typically include continuous sampling of NO, NO_x, and O_3, and collection of nearly-instantaneous, discrete, whole-air grab samples in stainless steel cannisters, for subsequent detailed analysis of VOC species. In a few rare field studies, time-integrated VOC samples have been collected in the aircraft over intervals ranging from 3-30 min. In many studies, ground level data of NO, NO_x, O_3 and VOC are also collected at surface stations. Ground level samples for VOC are commonly collected in plastic bags over an hour or more. Most past aircraft plume studies have been aimed at plume kinetics, and the sampling approach has involved cross-sectional sampling at multiple downwind sections in a quasi-Lagrangian mode. Owing to the time constraints imposed by such an approach, aircraft sampling at a given cross-section was limited typically to 1 to 4 horizontal cross-wind plume traverses at discrete elevations, and these were sometimes augmented by a vertical spiral through the plume to characterize the vertical distribution of the measured parameters. Occasionally, a background spiral was also made. VOC sampling, when included, typically consisted of 1 or 2 samples (grab or time-integrated) per cross-section. Horizontal aircraft plume traverses ideally included some time in the background on either side of the plume, thus providing background characterization of the continuously-measured species. Sampling of VOC in the background has typically been even sparser than in the plume.

The procedure and problems of cross-sectional integration are illustrated for the aircraft data of ozone measured continuously in the urban plume of St. Louis around noon on 18 July 1975, at a downwind distance of about 65 km from downtown (Gateway Arch). Figure 2 shows crosswind ozone profiles measured during aircraft traverses at three heights in the plume, which was spread vertically throughout the mixing layer extending to about 1000 m MSL; Figure 3 shows the vertical profiles of ozone as well as ambient temperature and "turbulence", measured during a vertical spiral through the same plume section. The turbulence parameter is a measure of the turbulent energy dissipation rate, and hence is a good indicator of small-scale turbulence.

The cross-sectional integration is performed in two steps: first, the crosswind integral or horizontal plume burden, $B_h(x, z)$, is evaluated for each traverse; next, the vertical integration of these burdens is performed. Mathematically,

$$B_h(x,z) = \int_{-\infty}^{\infty} [C(x,y,z) - C_b(x,z)]\, dy \quad , \tag{9a}$$

$$\text{and} \quad M(x) = \int_{0}^{H} B_h(x,z)\, dz, \tag{9b}$$

where H is the plume top (also the mixing layer height in the example presented here).

The evaluation of B_h requires the determination of the plume background concentration. In the example shown (Figure 2), the ozone concentration in each of the three profiles is higher at the left edge of the traverse than at the right edge. Also, the background ozone level appears to decrease with height. Figure 3 shows clearly the existence of a sharp, but thin, elevated inversion layer at about 1000 m MSL, which may be taken as the current mixing layer height. Turbulence (mixing) drops off sharply near the top of the mixing layer, as also does the plume ozone concentration. Figure 4 shows a plot of the vertical profile of B_h. The values corresponding to the three traverse profiles (shown as data points) were obtained by simple numerical integration (trapezoidal rule) of the continuous crosswind profiles (temporal resolution was about 1 second in the example shown), based on the assumption that the background value at each height was the lower concentration at the right edge of that profile. Such decisions concerning background levels must be made, and their implications must be clearly understood. The errors introduced into plume excess values by errors in choosing background levels are particularly severe for precursors and secondary species with large background values and relatively low emission fluxes (e.g. some less reactive VOC and ozone).

In order to perform the vertical integration of B_h (equation 9b), it is necessary first to complete the vertical profile of B_h in Figure 4 by interpolation between the three traverse values, and by extrapolation above and below. The spiral data (Figure 3) provide invaluable guidance in this step. First, plume top is clearly established by the presence of the elevated inversion layer, and by the sharp drop-offs in both the turbulence parameter and plume ozone. Based on the guidance of the spiral data, one may choose with reasonable confidence, the interpolations between data points, and the extrapolation at the top as shown in Figure 4. More subjective judgement is called for in performing the extrapolation between the lowest data point (~475 m MSL) and the ground. The spiral data only extend to a lower limit of about 400 m MSL (about 250-275 m AGL). The extrapolation shown assumes that plume ozone is uniformly distributed below this height. This is a reasonable assumption, given the convective conditions at mid-day on this clear summer day. Simultaneous measurement of ground level ozone at section x_d would clearly have been extremely useful in establishing a more reliable data point at ground level. This is important, because as much as 40% of the plume ozone mass is probably contained in this layer. In order to minimize P_{kin}, it is desirable to avoid sunny midday conditions. At other times of the diurnal cycle, however, the plume is likely to be even more concentrated near the surface, and surface level data are likely to be even more important. The problem in aircraft sampling of the inaccessibility of the lowest 500 ft or so is a serious one with respect to the mass balance method. It is important to minimize this height, and to include co-ordinated surface level measurements.

It is also clear that any fewer than three aircraft traverses, or traverses less optimally distributed, would have substantially reduced the reliability of the estimated value of the cross-sectional integral. In the light of the above illustration, it is clear that there are a

number of sources of uncertainty in the estimation of $M(x_d)$ even for a continuously measured species with detailed crosswind data. In the case of VOC, when the data base at a given cross-section consists of one or two point measurements only, the uncertainty in $M(x_d)$ is likely to be overwhelming. This is particularly so when the downwind sampling section is close to the urban boundary, and the actual crosswind concentration profiles of the VOC are very non-uniform. At present, it is not possible to measure all VOC species concentrations in a continuous mode. The high cost of analysis of samples prohibits the collection of very many samples. VOC data of a few grab samples are generally quite inadequate for a reliable mass balance application. In as much as concentration data are spatially integrated in the mass balance method, it is much more cost-effective and desirable to collect time-integrated samples for VOC analysis. Ideally, such time-integrated sample durations should be variable and tailored to capture source-specific portions of the overall urban plume.

The Reactive Plume Model for Estimating P_{kin}

For the present application, the model domain must be of metropolitan to mesoscale range. Within such a domain, the emission fields of VOC and NO_x, as well as the spatial distributions of VOC/NO_x and of the rate of the smog chemistry, are likey to be quite inhomogeneous. The chemistry is presumably strongly influenced by plume-plume and plume-background interactions. For a realistic simulation of such effects, a model with fine spatial resolution is necessary. For city-specific application of such a model, the flexibility of arbitrary crosswind resolution is desirable. Our model formulation is essentially hybrid: Lagrangian in transport, and Eulerian in crosswind resolution. The Lagrangian transport is within the context of the slab, but the slab is subdivided laterally into an arbitrary number of vertical pillars of varying widths. Figure 5 illustrates some of the model features. The upper figure shows the time-height (t-z) cross-section of the volume swept by the slab from 0600 to 2100, and the lower figure shows a horizontal plane extending laterally over the width of the metropolitan plume as it is transported between time t and $t+\Delta t$.

In the vertical plane, the model is resolved into two layers-- the mixing layer and the aloft layer. Each is well-mixed vertically. Each is modelled dynamically. The aloft layer composition changes by chemical reaction only. The mixing layer background concentration of each modelled species changes due to vertical dilution with entrained air from aloft during mixing layer growth, as well as due to chemistry and by dry deposition.

In the crosswind direction (Figure 5, lower), the metropolitan plume within the moving slab is resolved into N pillars, all of the same vertical extent as that of the plume bulk. All species are assumed to be uniformly distributed within each pillar, but the crosswind concentration profile of any species j at time t, i.e. $C_j(y, t)$, is free to be arbitrarily inhomogeneous and non-similar to that of any other species. The plume width W_p is discretized into the N segments at the time of initialization based on any rationalized scheme. Eulerian-type mass continuity equations for inidvidual species in each plume pillar, in the aloft layer, and in the background, provide the basic mathematical formulation for the instantaneous rate of change of the species concentration fields. The processes incorporated into the plume equations include source emissions, vertical dilution and entrainment of aloft air, dilution and entrainment/detrainment due to pillar expansion laterally, crosswind diffusion tending to smooth out lateral concentration gradients, chemical reactions, and ground removal. Boundary conditions at plume edges explicitly facilitate the entrainment into the plume of background air and aloft air.

The determination of the release time of a given plume parcel sampled downwind at t_d, and of its Lagrangian trajectory, are based on a plume Monte Carlo simulation technique[3]. Input

requirements include dynamic specification of the vertical plume transport layer and the wind data for this layer.

The Eulerian formulation involves the mass balance for each species in each cell of the moving vertical slab. The form of the mass balance equations, expressed in terms of species concentrations, are summarized below:

$$\left(\frac{\partial C}{\partial t}\right)_{i,j,} = \left(\frac{\partial C}{\partial t}\right)_{i,j,\text{ emission}} + \left(\frac{\partial C}{\partial t}\right)_{i,j,\text{ vertical dilution/ entrainment}} + \left(\frac{\partial C}{\partial t}\right)_{i,j,\text{ lateral dilution}} + \left(\frac{\partial C}{\partial t}\right)_{i,j,\text{ lateral entrainment/ detrainment}} + \left(\frac{\partial C}{\partial t}\right)_{i,j,\text{ lateral diffusion}} + \left(\frac{\partial C}{\partial t}\right)_{i,j,\text{ chemistry}} + \left(\frac{\partial C}{\partial t}\right)_{i,j,\text{ dry deposition}} \quad (10)$$

$i=1,2,3,\ldots,N$; pillars $\qquad j=1,2,3,\ldots,N_{sp}$ species

Details of each process term on the right side of the equation are given in Gillani (1986)[3].

The model is intended to be diagnostic. All meteorological variables are presumed to be measured inputs. Only the chemical variables, i.e. the species concentrations, are the subject of model calculations. In the current version of the model, only gas-phase chemistry is included. The model is flexible enough to accept any of the commonly implemented chemical schemes. They may be based on molecular reactivity type classification of the VOC or on the carbon-bond type classification. Removal by dry deposition is parameterized in terms of the deposition velocity concept and is included for SO_2, NO_2, O_3, HNO_3, PAN and H_2SO_4 only. Removal of any other modelled species can easily be included if reliable information concerning deposition velocity of such species is available. Currently, such data are not available for VOC. Hence, ground loss of VOC may add to the uncertainty of the emissions estimates based on the mass balance analysis.

Implementation of the Mass Balance Method

The application of the mass balance procedure would proceed as follows (with reference to equation 7):

a) estimate $M(x_u)$, $M(x_d)$ from measured concentration data of the precursors;

b) estimate P_{kin} and $\langle Q/u_0 \rangle$ for the precursor species iteratively, as outlined below: Starting with the current urban emission estimates, the model would be run from t_u to t_d (x_u to x_d), using the measured upwind and background chemical conditions, and meteorological and plume dynamics variables. At each integration time step of the model run, $(\partial C/\partial t)_{chem}$ would be evaluated for each precursor species in each pillar, and this quantity would then be integrated for the whole plume slab. Such spatially integrated chemical terms would be accumulated for the whole model run from t_u to t_d, and would result in P_{kin}. Combining this P_{kin} with the empirically determined value of ΔM would yield an updated value of $\langle Q/u_0 \rangle$, and hence of $q(x, y, t)$. A new P_{kin} would then be evaluated corresponding to the updated emission field. Such successive updates of P_{kin} and of Q would be continued, until the iteration converged

and yielded the final estimate of Q_{urban} consistent with the measured ΔM.

PRINCIPAL DESIGN CRITERIA FOR MASS BALANCE FIELD STUDY

The integral mass balance equation for any species is:

$$\left\langle \frac{Q}{u_0} \right\rangle_{urban,j} = [M(x_d) - M(x_u)]_j - \left[\left\langle \frac{Q}{u_0} \right\rangle_{up-wind,j} + \left\langle \frac{Q}{u_0} \right\rangle_{down-wind,j} \right] - P_{kin,j} \qquad (11)$$

The principal objectives in designing a field study specifically for the purpose of estimating urban emissions of NO_x and VOC by the mass balance method are:

a) to minimize the contribution of the upwind and downwind source terms;
b) to minimize the contribution of the kinetics term;
c) to maximize the accuracy of the empirical term, ΔM;
d) to maximize the accuracy of the u_0-estimate;
e) to achieve the appropriate spatial, source-type, and species resolution, and temporal coverage.

The best way to minimize the upwind and downwind source terms is by locating the upwind and downwind sampling locations as close to the corresponding urban boundaries as possible. If significant upwind and/or downwind sources do exist, sub-experiments may be necessary to quantify their specific source contributions. Minimization of the stretch $(x_d - x_u)$ will also control P_{kin}. Further control of P_{kin} may be exercised by avoiding wet conditions, bright sunny periods, polluted background, and intense mixing.

The following considerations influence the accuracy of estimation of $M(x_d)$:

a) Accuracy and spatial-temporal resolution of measurements of NO_x and VOC species concentrations. NO and NO_x can be measured continuously with high precision and accuracy (~90%) at concentrations above 5 ppb, using the standard chemiluminescence analysis. It is highly desirable to make at least some measurements, particularly in the background, with special NO_x analyzers with sub-ppb sensitivity. Continuous analyzers for non-methane organic compounds (NMOC) are widely used at surface stations, but are unreliable at concentrations below 500 ppbC.[14] Typical concentrations in the upper air are below 100 ppbC even in urban plumes. Also, continuous NMOC analyzers do not provide speciation. The measurement of individual VOC species concentrations is a complex process [15]. Air samples are normally collected in plastic bags at surface monitoring stations over periods of 1-3 h, and as grab samples in stainless steel cannisters in aircraft. Cannister samples are preferred because sample contamination is less likely, samples are more stable, and can be transported more easily. Detailed chemical analysis of the samples is based on GC speciation, which requires sophisticated analytical equipment, high level of operator skill and experience, and considerable time. It is expensive. Consequently, VOC sampling is done very sparingly in practice, and even the best of the existing aircraft sampling data bases consist of scanty point measurements only. For a targetted mass balance field study, time-integrated samples of variable intervals corresponding to full traverses, as well as source-specific subsets of traverses, are much more desirable than grab samples. It is now feasible to do such time-integrated sampling using cannisters [5,14]. With proper care, it is possible to obtain VOC measurements for most species with accuracy comparable to that of NO_x measurements.

b) Adequacy of background measurements. For reactive species, background concentrations are

likely to be low, and the uncertainty in their measurement is likely to be high. For less reactive species, background levels are likely to be higher, and while their measurement uncertainty is likely to be relatively low, even small percentage errors may potentially cause large errors in $M(x_d)$, particularly when plume excess over background is small (e.g., for large x_d and small Q). Background measurements must be done with the highest possible sensitivity, precision, and accuracy.

c) Location and spatial-temporal coverage of aircraft sampling. The sampling sections must be selected as close as possible to the boundary of the urban source region, and sampling must be approximately Lagrangian. Particular attention must be paid to maximum spatial coverage in downwind sampling. As many traverses as possible must be made, and these must be spaced appropriately to capture as much of the cross-sectional mass as possible. Co-ordinated surface measurements in ground level traverses are highly recommended. Aircraft spirals must descend as low as possible. Vertically-integrated measurements from upward-looking, remote-sensing instruments (e.g. COSPEC) in mobile surface platforms may also provide useful supplementary information. In the integral mass balance, there is no term which explicitly incorporates vertical mass fluxes. For proper integral mass balance, the vertical range of upwind and downwind sampling must be the same, and sufficiently high that vertical fluxes across the top of the "box" are negligible. Conditions conducive to large vertical mass transport must be avoided.

Meteorological Measurements

The two most critical meteorological quantities for mass balance analysis are the wind field and the mixing height. Transport winds over the emission area are required in the analysis of the source terms $\langle Q/u_0 \rangle$. The Monte Carlo transport simulation which determines the emission time as well as trajectory and spread of the sampled plume requires as input the upper air winds over the full stretch of emission transport to x_d. The delineation of plume top over the source area is necessary in the determination of $u_0(x,t)$. Lidar measurements of the vertical distribution of aerosols may prove very useful for this. Aircraft spirals data of temperature and turbulence are also invaluable for fixing mixing height. Other meteorological data of interest include vertical profiles of ambient temperature and humidity, and the intensity of broad-band and UV solar radiation.

Source-Type Resolution

It is useful to estimate not only the aggregate emissions of NO_x and VOC, but also source-specific emissions. Special experiments may be targetted to study emissions from particular major sources, and source types. Tracers may be used for this purpose. Tracers may be natural (e.g. ethane from commercial natural gas sources, propane from liquified petroleum gas sources, benzene and toluene from solvent evaporations, n-butane and i-pentane from gasoline vapors, etc.), or artifical. For example, highway emissions of VOC were estimated using controlled SF_6 tracer releases from a vehicle travelling in traffic.[16z] The analysis was based on the ratio of measured concentrations of VOC and SF_6, and the known release rate of SF_6. Sources may be isolated for study using the aircraft data at x_d under particular transport conditions when specific major source plumes are aligned in parallel transport. Specific source types can also be identified based on receptor modeling in conjunction with ambient measurements of elemental composition.

THE APPLICATION DATA BASE

Urban plume field studies involving upwind/downwind aircraft measurements have

been carried out in many metropolitan areas in eastern North America in the past 15 years. For some of these cities, special effort has also been made in developing more detailed emission inventories than are generally available as part of the standard NEDS or NAPAP data bases. The available field and emissions data bases of Houston, Atlanta, St. Louis, Columbus, Chicago, Milwaukee, Sarnia (Ontario), the Boston-New York City Corridor, Philadelphia, Baltimore-Washington, and the Rhein-Ruhr industrial area of W. Germany were surveyed and assessed for use in this project. The more desirable time-integrated aircraft sampling of VOC was performed only in the two non-U.S. studies (viz., Sarnia and Rhein-Ruhr). Sample contamination problems and inadequate vertical coverage eliminated the Sarnia study from further consideration. Of the U.S. studies, the following four were finally chosen:

i) the MISTT/RAPS studies in St. Louis (1974-76);
ii) the PEPE/NEROS study in Columbus (1980);
iii) the NEROS study in Baltimore-Washington (1980);
iv) the Atlanta study (1981).

Collectively, the four selected locations provide a broad geographical coverage of the eastern U.S. From the point of view of detail of emissions inventory, they also cover the full spectrum. In each case, the emissions inventory and field study are referred to nearly the same time frame (±1 year). All four studies were sponsored by EPA. A brief overview of pertinent aspects of the four selected data bases is presented below.

Mass balance was the central design concept of Project MISTT, which was mainly a meso-scale field measurements program aimed at quantifying the dynamics and kinetics of sulfur emissions from large point and area sources in St. Louis[17,18]. Cross-sectional aircraft sampling was performed in the plumes at multiple downwind locations, with increasing emphasis on farther-out distances in the latter years (1975, 1976). Co-ordinated supporting measurements included ground-level sampling from mobile vehicles, and upper air wind measurements. The measurements were carried out in the summers of 1974, 1975, and 1976. MISTT ran concurrently with RAPS (Regional Air Pollution Study, 1974-77), which was a metropolitan-scale study with a focus on ground-level air pollution monitoring in a 25-station network operating continuously for 3 years[19]. Supporting measurements in RAPS included surface and upper air meteorology, and an extensive program of vertical aircraft (helicopter) spirals. An urban emissions inventory effort of unmatched scope (in terms of spatial detail) was carried out. Many special experiments were performed in conjunction with RAPS during several intensive measurement periods.

The heart of MISTT was the aircraft measurement program. An elaborately equipped aircraft[20] measured NO, NO_x, O_3, SO_2, and a variety of aerosol, meteorological, and navigational parameters continuously. The NO_x data base of MRI is excellent. Grab samples were collected for detailed VOC analysis only in 1976, and even then the data base is too sparse for reliable mass balance analysis.

A principal objective of RAPS was to generate a data base for evaluating urban photochemical models. To this end, a major effort was mounted to compile a detailed emissions inventory of SO_x, NO_x, and VOC. The VOC inventory includes a breakdown by Source Classification Codes, and also by reactivity classes (paraffins, olefins, aromatics, and aldehydes). Temporal resolution is down to 1h. The spatial resolution varies from 1 km square grid cells in the urban core to cells of 10 km sides at the metropolitan boundaries. This compares with the standard grid resolution of approximately 20 km in the NAPAP 1980 Emissions Inventory. The inventoried region covers an area in excess of 5000 km^2. The surface monitoring network stations also cover this region, with maximum density in the urban core. The network data, at a temporal resolution of 1 h, include NO, NO_x, O_3, THC, CH_4, and CO measured

continuously at all stations, and bag samples for VOC analysis were also collected at all stations. The common meteorological variables were measured at all stations; some stations also had 30 m met towers. In addition, upper air met measurements (including wind speed and direction every hour during the daytime) were made at four fixed sites. Supplemental measurements were made during summer intensives.

The MISTT/RAPS data base is one of the best in existence for estimating urban NO_x emissions, both aggregate and by source-type, based on the mass balance method. It should also prove invaluable in testing the power and limitations of the method. The data base, like all existing urban data bases of aerial measurements, is most probably inadequate for reliable estimation of VOC emissions.

A major field study with a dual goal was conducted in the summer of 1980 out of Columbus, OH.[21] The focus of PEPE was on regional haze episodes, while NEROS (Northeast Regional Oxidant Study) was focussed on urban plume studies. Five *in-situ* chemical sampling aircraft and two mobile ground vehicles measured O_3, NO, NO_x, and collected VOC grab samples as well as filter samples which were analyzed for sulfates and nitrates. Three surface monitoring stations (typically upwind, downtown, and downwind) measured O_3, NO, NO_x and collected time-integrated VOC bag samples (analyzed for VOC species including aldehydes). Many other chemical and meteorological variables were also measured. Aircraft flight patterns included standard crosswind traverses and spirals in the urban plume at multiple downwind sections. The VOC data base of PEPE/NEROS is richer than that of MISTT, but probably still too meager for reliable VOC mass balance analysis.

Measurements were also made in the Baltimore-Washington area as part of NEROS in the summer of 1980. The East Coast urban plume studies of NEROS were carried out in conjunction with NECRMP (Northeast Corridor Regional Modeling Project)[21]. Measurements similar to those in the Columbus program were made from three *in-situ* chemical sampling aircraft, a mobile ground vehicle, and a network of surface monitoring stations.[23] A special emphasis was placed on VOC sampling, analysis and quality assurance in this study. The VOC data base is among the most substantial of all existing aircraft data bases. Yet, in 250 hours of total flight time, the three aircraft only collected a total of 225 grab samples (point measurements). The available emissions inventory of VOC and NO_x for Baltimore-Washington, as well as for Columbus, is part of the 1980 NAPAP Emissions Inventory, which has a spatial resolution of about 20 km.

An oxidant study based on aircraft sampling was carried out in Atlanta in July 1981.[6] One standard instrumented aircraft and six ground monitoring stations collected the chemical data. Pertinent meteorological measurements, including upper air winds, were also made. Aircraft and ground measurements included NO, NO_x, O_3, VOC (C_2-C_{10}), and halocarbons. Aircraft measurements of VOC are based on grab samples in stainless steel cannisters. The VOC data base, as in other studies, is inadequate for mass balance analysis. The flight plan typically involved upwind measurements in the morning, and downwind measurements at about 50 and 70 km from the urban core in the afternoon.

CONCLUSION

A shroud of doubt cloaks current estimates of urban emissions of NO_x and VOC, particularly VOC. Direct checks on the accuracy of these emissions estimates are not practical. An indirect reliable approach based on ambient measurements of these precursors of acidic depositions, regional haze, and photochemical smog is needed. The mass balance method, based on characterization of upwind inflow and downwind outflow of these precursors relative

to an urban source area, is potentially such an approach.

A Lagrangian formulation of the mass balance approach has been outlined. Its implementation is semi-empirical in nature. Empirical data are required for the concentration distribution of the precursors over the inflow and outflow sections, and for boundary layer and urban plume dynamics. The role of plume kinetics is to be estimated by means of a reactive plume model with arbitrary crosswind resolution. The principal criteria for the design of a field measurement program to generate the needed data base are outlined, and the main sources of uncertainty in the empirical data and their use in the analysis are identified.

A brief overview is presented of four existing urban field data bases selected for trial application within the context of mass balance analysis for estimation of emissions of NO_x and VOC. Preliminary indications prior to actual implementation of the application are that the existing data base of VOC ambient concentrations is probably quite inadequate for a reliable estimation of urban VOC emissions, but that the corresponding NO_x data base may be sufficient at least to test out the methodology and the major sources of uncertainty in its implementation. Owing to the fact that downwind sampling in the existing data bases is far from optimal in terms of its location, timing, spatial-temporal resolution, and measurement accuracy, it is expected that the corresponding analyses based on these data bases will be handicapped by an exaggerated role of such extraneous effects as plume kinetics. As such, the analyses to be attempted represent worst-case scenarios. It is believed, however, that a substantially improved and cusomized field data base is possible to obtain in a future targetted field study, and may possess the potential for yielding much improved and acceptable estimates of urban emissions of NO_x and VOC not only on an urban aggregate basis, but even perhaps at finer spatial, temporal, source-type, and species levels. The analyses based on the existing data bases, it is hoped, will provide greater insight into the possibilities and limitations of the mass balance approach for the purpose at hand, and may provide a basis for the formulation of a design of the targetted future field study.

REFERENCES

1. J . S. Ching, J.H. Novak, K.L. Schere and N.V. Gillani, "Reconciling urban VOC/NO_x emission inventories with ambient concentration data," paper No. 87-58.3, 80th Annual Meeting, APCA, New York, NY (1987).

2. N.V. Gillani and W.E. Wilson, "Formation and transport of ozone and aerosols in power plant plumes," *Annals N.Y. Acad. Sci. 338,* 276-296 (1980).

3. N.V. Gillani, "Ozone formation in pollutant plumes: development and application of a reactive plume model with arbitrary crosswind resolution," *EPA Report* (In press).

4. C.M. Benkovitz, "Uncertainty analysis of NAPAP Emissions Inventory," paper presented at the *Second Annual Acid Deposition Emission Inventory Symposium* , Charleston, SC, (Nov. 1985).

5. H.G. Richter, F.F. McElroy, and V.L. Thompson, "Measurement of ambient NMOC concentrations in 22 cities during 1984," paper No. 85-22.7, *78th Annual Meeting, APCA* , Detroit, MI (June 1985).

6. H. Westberg and B. Lamb, "Ozone production and transport in the Atlanta, GA region," *Washington State University Report to EPA* (1985).

7. J.L. Haney and C. Seigneur, "Investigation of reactive hydrocarbon to NO_x ratio in the South Coast Air Basin," Technical Memorandum, Systems Applications, Inc., San

Rafael, CA (31 Dec 1985).

8. W.H. White, R.B. Husar, D.L. Blumenthal, and D.S. Ensor, "Los Angeles smog aerosol dynamics derived from spatio-temporal distribution data," paper presented at the *Annual Meeting of the ACS*, Chicago, IL (1973).

9. R.B. Husar, J.D. Husar, N.V. Gillani, S.B. Fuller, W.H. White, J.A. Anderson, W.M. Vaughan, and W.E. Wilson, "Pollutant flow rate measurement in large plumes: sulfur budget in power plant and area source plumes in the St. Louis region," paper presented before *Div. Environ. Chem., Annual Meeting of the ACS*, New York City, NY (1976).

10. W.H. White, J.A. Anderson, D.L. Blumenthal, R.B. Husar, N.V. Gillani, J.D. Husar, and W.E. Wilson, "Formation and transport of secondary air pollutants: ozone and aerosols in the St. Louis urban plume," *Science 194*, 187-189 (1976).

11. N.V. Gillani, J.D. Husar, and D.E. Patterson, "Project MISTT: kinetics of particulate sulfur in a power plant plume out to 300 km," *Atmos. Environ. 12*, 589-598 (1978).

12. N.V. Gillani, "Project MISTT: mesoscale plume modeling of the dispersion, transformation, and ground removal of SO_2," *Atmos. Environ. 12*, 569-588 (1978).

13. W.H. White, D.E. Patterson, and W.E. Wilson, "Urban exports to the non-urban troposphere: results from Project MISTT," *J. Geophys. Res. 88*, 10745-10752 (1983).

14. F.F. McElroy, V.L. Thompson, and H.G. Richter, "A Cryogenic Preconcentration - Direct FID (PDFID) method for measurement of NMOC in ambient air," *EPA-600/54-85/063* (1985).

15. H. Westberg, W. Lonneman, and M. Holdren, "Analysis of individual hydrocarbon species in ambient atmospheres: techniques and data validation," in *Identification and Analysis of Organic Pollutants in Air*, Ann Arbor Sciences (publ.), Boston, MA, pp. 327-337 (1983).

16. R.B. Zweidinger, J.E. Sigsby, S.B. Tejada, F.D. Stump, D.L. Dropkin, and W.D. Ray, "Detailed hydrocarbon and aldehyde mobile source emissions from roadway studies," *Unpublished EPA Report* (1986).

17. W.E. Wilson, "Sulfates in the atmosphere: a progress report on Project MISTT,"*Atmos. Environ. 12*, 537-547 (1978).

18. N.V. Gillani and W.E. Wilson, "Project MISTT: Measurements and Data Base," *EPA Report, 3 Volumes* (In Press).

19. J.A.Strothman and F.A. Schiermeier, "Documentation of the Regional Air Pollution Study (RAPS) and related investigation in the St. Louis AQCR," *Technical Report, EPA-600/4-79-076* (1979).

20. D.L. Blumenthal, J.A. Ogren, and J.A. Anderson, "Airborne sampling system for plume monitoring," *Atmos. Environ. 12*, 613-620 (1978).

21. N.V. Gillani and F. Pooler, "Project PEPE-NEROS (1980): Measurements and Data Base – An Overview," EPA Report (In Press).

22. N.C. Possiel and W.P. Freas, "NECRMP - Description of the 1980 urban field studies," *EPA-450/4-82-018* (1982).

23. Brookhaven National Laboratory, *NEROS 1980 Data Characterization, Vols A,B,C,D,E,F,G*, BNL Reports to EPA (1982).

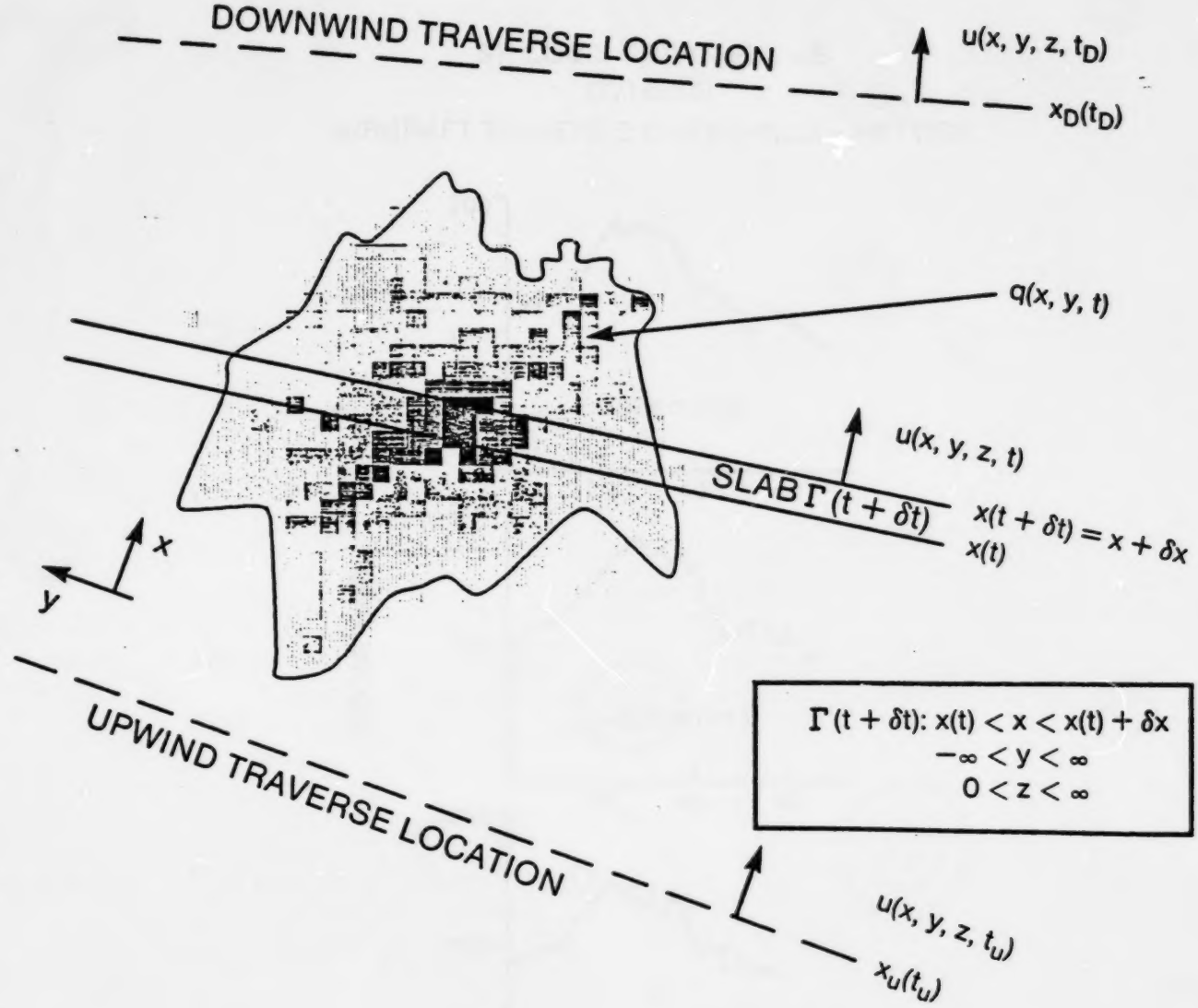

Figure 1. URBAN MASS BALANCE CONCEPT
Definition of Variables.

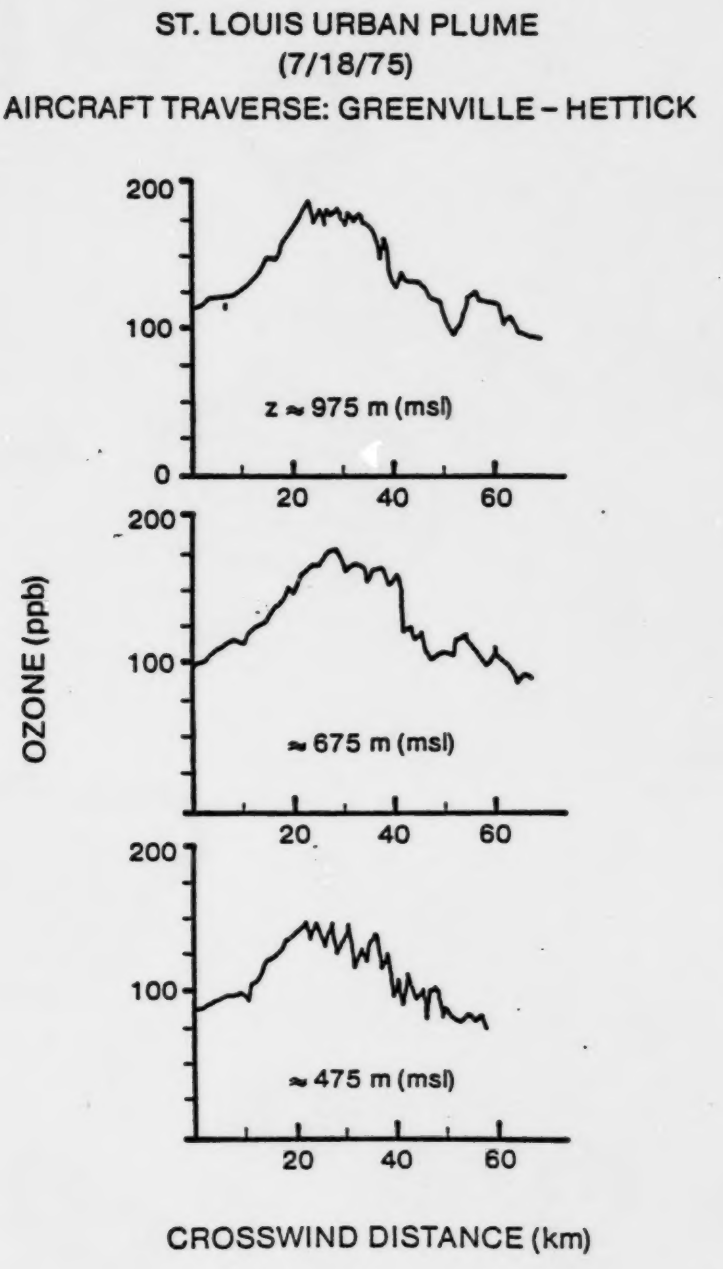

Figure 2. Crosswind data of ozone for three MRI aircraft traverses across the urban plume of St. Louis on 18 July, 1975, at a cross-section about 65 km downwind of the urban core (Gateway Arch).

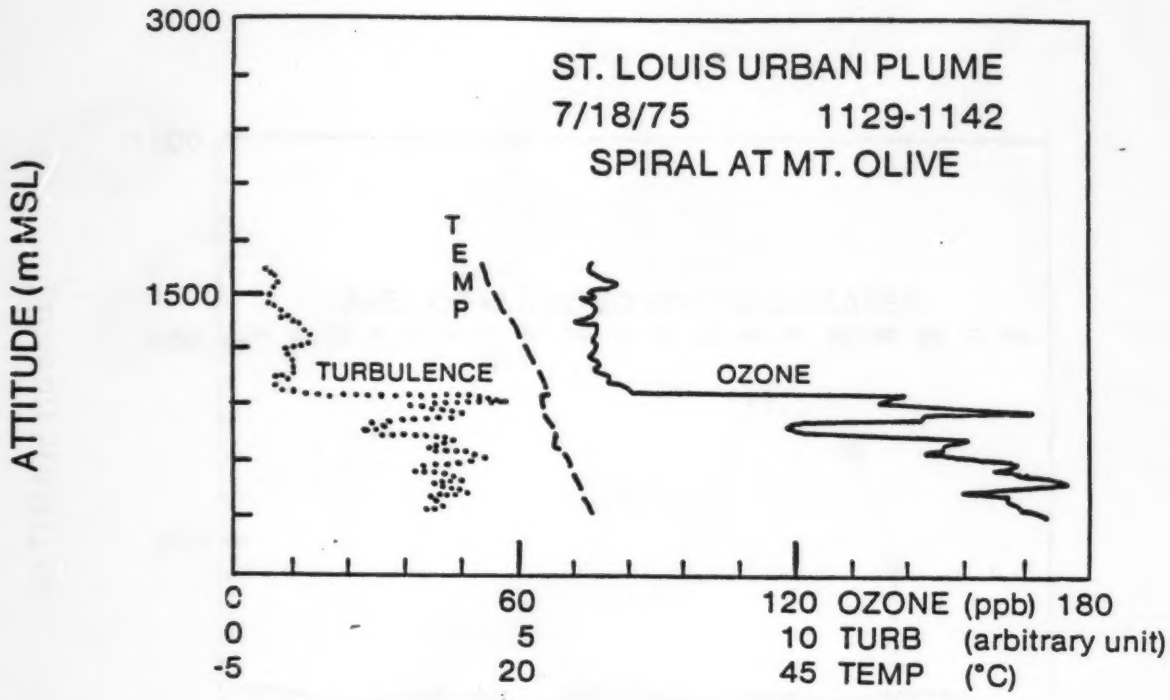

Figure 3. MRI aircraft spiral data through the urban plume of St. Louis on 18 July, 1975, at a cross-section about 65 km downwind of the urban core (Gateway Arch).

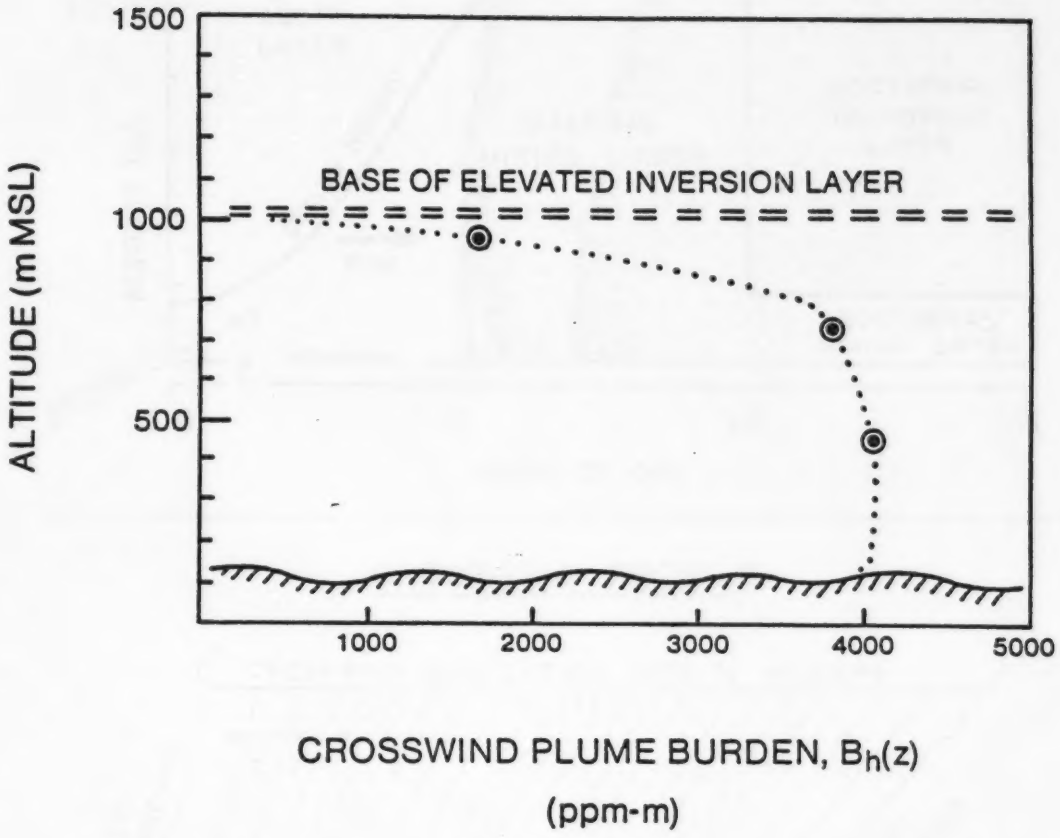

Figure 4. Crosswind integrals of excess plume ozone for the three MRI aircraft traverses across the urban plume of St. Louis on 18 July, 1975, at the 65 km downwind cross-section.

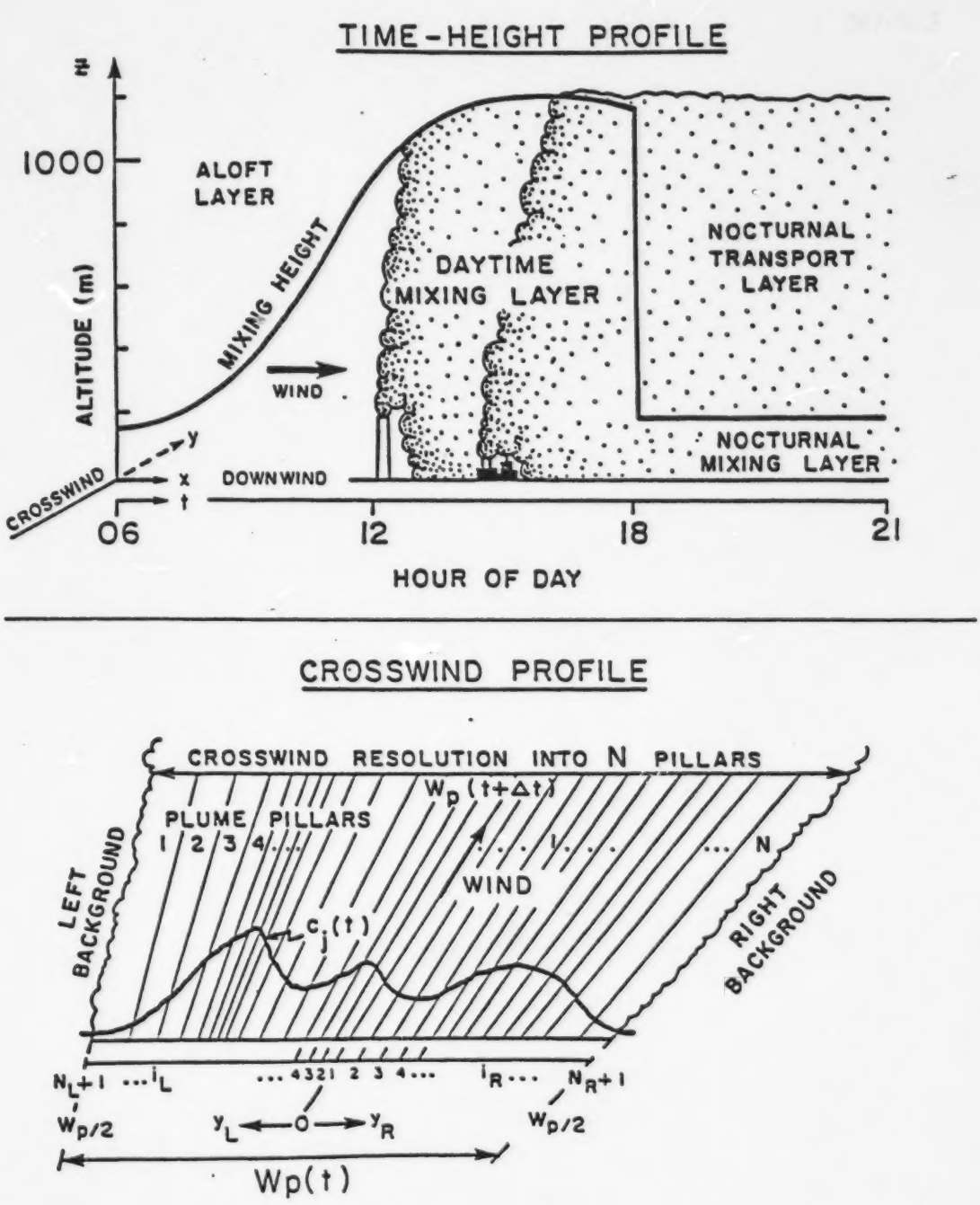

Figure 5. Illustration of some spatial-temporal features of the model in the vertical t-z plane (upper), and the horizontal t-y plane (lower).